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Laboratory investigation on the evaluation of crude oil concentration by spectroscopic methods

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Abstract

A transmission spectroscopy approach for the evaluation of water and oil concentration in crude oil has been investigated at the IMRI laboratories. Transmission spectra of crude oil and water samples of typically 1 mm-thickness were taken with our FTIR spectrometer. The possibility of extending such measurements to an in-situ device as well as the expected accuracy are discussed.

1. INTRODUCTION

A spectroscopic approach for the in-situ evaluation of oil and water concentration in crude oil was proposed to P. Cielo by S. Boyer, from Esso Resources in Calgary, at the Digicom '87 ISA Conference in November '87. P. Cielo and K. Cole accepted to carry out a laboratory investigation on such a possibility using some crude oil and water samples shipped to IMRI by Esso Resources. This report describes the results of our investigation.

2. DESCRIPTION OF THE PROBLEM AND OF DIFFERENT POSSIBLE METHODOLOGIES FOR ITS SOLUTION.

Measurement of oil and gas concentration in the liquid extracted from wells is required for taxation purposes. The liquid is extracted as a mixture of, mainly, oil and water, with a certain amount of methane which at the underground hydrostatic pressure of several thousand psi is mostly dissolved both in oil and in water.

The usual approach to determine the percentage of oil, water and methane gas out of the well is to depressurize the liquid and introduce it in large decanters where the three phases separate, after which the proportion of each phase is evaluated manually, with a precision of the order of 2%. Methods which are faster and which do not require depressurization of the crude are actively sought by the extraction companies in order to automate and speed up the process.

One approach which is successful only to a limited extent uses a capacitive probe measuring the dielectric properties of the oil-water mixture. Such a method fails, in particular, for higher concentrations of water. When the mixture can be considered as an emulsion of oil bubbles in a water matrix, electrical conduction shorts out the condenser plates so that no meaningful signal can be obtained. A similar instrument operating at higher frequencies has been developed by a U.S. company to avoid such problems, but the results have been deceptively inaccurate. An

approach using still higher frequency (microwave) radiation is now under investigation where the microwave frequency is chosen to correspond either to a water or to an oil absorption band, and the amount of heating is monitored to evaluate the concentration of the two components.

Electrical methods are potentially conducive to simple in-situ sensors but, apart from the drawbacks mentioned above, they are not attractive for this kind of applications because of safety concerns. Electrically inert techniques such as spectroscopic methods would be much more convenient for routine automated measurements. Other off-line chemical analysis techniques such as liquid chromatography, mass spectrometry etc. are too slow and not sufficiently rugged for a continuous on-site evaluation. This report summarizes our laboratory results which were performed to evaluate the spectroscopic approach.

3. SPECTROSCOPIC ANALYSIS

Several samples of crude oil were analyzed in transmission with our Nicolet FTIR spectrometer, using cells with windows of either potassium bromide or barium fluoride. Figure 1 shows the spectrum of a "Bahia" highly viscous crude oil sample which we received from John Prinsen of our institute. The absorption bands visible in this spectrum, most of which are related to the C-H links in the heavy oil chains, are not dissimilar to the spectral features of polyethylene (see App. I, Fig. 37).

A number of considerations can already be made on the basis of this spectrum. The choice of a near-IR spectral region is preferable for this kind of application for a number of reasons:

(a) The near-IR bands, such as those in the 5800 cm^{-1} and 4300 cm^{-1} areas, are characterized by a lower absorptivity than the fundamental bands such as the one near 2900 cm^{-1}. The near-IR bands are thus preferable to obtain a suitable absorptivity signal with a conveniently large cell thickness. Cell thicknesses of the order of 1 mm or more are desirable for on-line applications to avoid plugging or excessive segregation problems.

(b) A near-IR operation is also desirable because of the possibility of using more rugged and thermoelectrically-cooled detectors (see Ref. 1, Sect. 3.3.3; the spectra shown in this report were obtained with a cryogenically cooled HgCdTe detector) and light sources of higher spectral radiance (see Ref. 1, Figs. 3-4 and 7-11).

An in-situ oil concentration analyzer could be devised by monitoring the depth of the 5800 + 100 cm^{-1} absorption band with a known cell thickness of, say, 1 mm and using Beer's law. Apart from the usual sources of error implicit in this approach (see Ref. 1, Sect. 8.3.1), a concentration analysis based on this approach assumes that the depth of the absorption band is uniquely related to the oil concentration for any composition of the crude oil. Although a systematic analysis of different kinds of oil could not be made because only one oil type was shipped by Esso, it is felt that oils with different paraffinic contents should have slight differences in their absorption spectrum which would cause variations in the absorption coefficient used in Beer's law computations. Such a problem could possibly be avoided by an in-situ preliminary calibration to be made for each oil well installation, assuming that the chemical composition is constant throughout each well.

To gain some appreciation for the compositional factor, near-IR spectra of the kind shown in Fig. 2 were taken with the Esso-supplied sample and compared to the IMRI-available sample shown in Fig. 1. Although some slight differences are visible, e.g. in the 4000 to 4200 cm^{-1} region, the two main near-IR absorption bands are very similar, and their depth corresponds, within the precision with which the cell thicknesses were known, to the variation of the path length for the two different samples.

The next question is whether one can differentiate the spectral absorption bands of the oil and of water to allow an evaluation of the concentration of both components. Fig. 3 shows the transmission sample of demineralized water. An essentially identical spectrum was obtained with the natural water sample shipped by Esso. The two main near-IR absorption

bands are found in the 7000 cm^{-1} and 5200 cm^{-1} regions, which are well separated from the 5700 cm^{-1} and 4300 cm^{-1} bands due to oil. A separation of the spectra of these two components is thus possible in the near-IR area.

Based on the results shown in Figs. 2 and 3, the two spectra were numerically superposed to simulate a 50:50 oil-water mixture with different path lengths through the cell. The results are shown in Fig. 4. It can be inferred from this analysis that a good choice for an oil-water concentration evaluation would be to sample the transmissivity at 5800 $\pm$ 100 cm^{-1} for oil and 6900 $\pm$ 200 cm^{-1} for water with a common reference at 6100 $\pm$ 100 cm^{-1}. Three-detector nondispersive analyzers of the kind described in App I for the evaluation of polyethylene film thickness could be adapted to this application. The polyethylene thickness analyzer technology described in App. I has been transferred from IMRI to the instrumentation company Exfo/Opsys of Québec City which might be available for collaboration with IMRI's assistance.

Before the projected results shown in Fig. 4 can be extended to a real oil-water emulsion, information about the typical distribution of the respective phase size should be made available by Esso. One possible problem which may be encountered with oil-water emulsions of very fine size is illustrated in Fig. 5. A 50:50 oil-water mixture was stirred in a blender to obtain droplets in the 1 to 50 µm range. A first problem is the low transmittance of such a sample due to multiple scattering at the oil-water interfaces, resulting in a very poor signal to noise ratio. A second problem is the spectral dependance of the attenuation through a sample containing particles whose diameter is of the order of magnitude of the light wavelength (see App. I, Fig. 40). This latter effect can be noticed by comparing the 7600 to 7000 cm^{-1} ranges of the spectra shown in Figs. 4 and 5. To avoid an undesirable dependence of the transmittance on the droplet size, such a size should be prevalently larger by a factor of 10 or more compared to the typically 2 µm wavelength.

A further question which was addressed is the possibility of evaluating the methane content by using a similar approach. Methane molecules have a fundamental band absorption in the 3000 cm^{-1} area (see, e.g., Ref. 2, Fig. 4). Such a band is thus substantially confused with the strong 2900 cm^{-1} absorption from the oil. An overtone around 6000 cm^{-1} (see Fig. 6) might be discernible as a shoulder on the wider 5800 cm^{-1} oil absorption band by using an additional narrow-bandwidth filter. The line structure extending from 5900 to 6150 cm^{-1} which is visible in the gaseous-phase spectrum of Fig. 6 will no longer be discernible if methane is dissolved in either the oil or the water liquid phase. The methane concentration should, however, be substantially large to produce an absorption band of significant amplitude. It should be noted that the gas-phase spectrum shown in Fig. 6 was obtained with a 500 mm path length. If gaseous methane is present in the crude at close to ambient pressure, it might be possible to determine its volume by exclusion from the measured amounts of oil and water.

4. DISCUSSION

As mentioned above, a realistic in-situ spectroscopic concentration sensor should use rugged and sensitive detectors and reliable light sources. The spectra reported here were taken using a liquid-nitrogen cooled HgCdTe detector and a 1500°C thermal source, and a certain amount of time averaging was required to upgrade the signal-to-noise ratio. By restricting the spectral range to the near-IR area, optical detectors can be used having sensitivities larger by nearly two orders of magnitude in this spectral region (see Ref. 1, Fig. 3-23), while higher brightness tungsten-halogen lamps may be adopted. A three-wavelength system of this kind which was developed by IMRI and transferred to Exfo/Opsys of Québec City could be made available by this company for further tests. Their sensor is commercially available at nearly $20,000.

A number of questions should, however, be clarified before committing to further investigations. As Fig. 5 above shows, a dramatic reduction of light throughput takes place if the liquid is in the form of a fine-

structured liquid emulsion. A similar attenuation would be observed for a gas-in-liquid emulsion as might occur if the dissolved methane segregates in gaseous bubbles as the crude oil is pumped from the high underground hydrostatic pressure to a lower pressure above ground. Such a problem might require further pressurization of the sample before analysis.

Another question is related to the possible variations of spectral characteristics for different kinds of crude, to evaluate whether a well-by-well calibration is required. Although the two samples tested had similar spectral characteristics, a systematic analysis should be performed to evaluate the degree of repetitivity of the spectral features on a complete set of the crude oil kinds handled by Esso Resources. Samples of oil originating from different levels inside the well should also be analyzed to verify whether the composition may change within the same well because of sedimentation mechanisms.

The mechanical design of an in-situ system should be the object of studies and discussions in parallel with the laboratory investigation to make reasonably sure that a viable sampling approach is possible for the relatively small cell thicknesses which are mentioned above. The sampled volume could either be within the pipe, using two quartz windows or a fiber-optic bundle face-to-face in the flowing liquid, or else a reduced-flow sampling pipe would be used to divert part of the crude to the analyzer. The latter approach is more cumbersome but it is preferable to the direct viewing configuration in terms of easier cleaning and maintenance, as well as a lower probability of viscosity-dependent phase segregation. Fiber-optic probes are particularly attractive for safety considerations, but they introduce light losses of typically 10 d^R on the transmitted light throughput.

The projected accuracy of an oil-in-water spectroscopic sensor may be severely affected by a number of factors such as the emulsion phase distribution, compositional changes, dirt accumulation or the presence of additional phases as described above. Other sources of error due to elec-

tronic noise, light source aging or nonuniform spectral absorptivity within the sampled spectral range (see Ref. 1, Fig. 8-27) are also present. Even for a relatively well-behaved material such as a polyethylene film, our experience as reported in App. I indicates that the level of accuracy is within a few percentage points. The obtention of a 2% concentration accuracy in the monitoring of crude oil is thus believed to be unlikely.

5. CONCLUSION

A spectroscopic approach for oil-in-water concentration monitoring was investigated using the IMRI FTIR spectrometer. The near-IR spectral features resulted to be relatively favorable to such an approach, because of the good separation of the oil and water spectral bands. Questions still to be investigated are related to the size distribution of liquid-liquid or gas-liquid emulsions in crude oil, compositional uniformity and the mechanical design of an in-situ device. If Esso Resources feels that the above results justify a second step of investigations, IMRI will be available for further spectroscopy studies or for assistance to an instrumentation company.

An alternative approach, ultrasonic velocimetry, a field in which some of our colleagues at IMRI have gained a large amount of experience, might be more appropriate than spectroscopy for this application. Because of its longer wavelength, ultrasound would be less affected by attenuation from small bubbles, while larger cell sizes could be used. Problems similar to the ones mentioned above are however expected in terms of the dependence on oil composition, while an independent evaluation of the crude temperature and pressure would probably be necessary. Dr. Jean Bussière, to whom the Esso oil samples have been made available, has suggested this alternative and will eventually contact Esso to discuss such a possibility.

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2. R. M. Durham, "Process gas analyzers using NDIR" Proc. SPIE vol. 411, p. 72 (1983).

3. J. P. Dakin et al., "A novel optical fibre methane sensor" Proc. SPIE vol 734, p. 254 (1987).

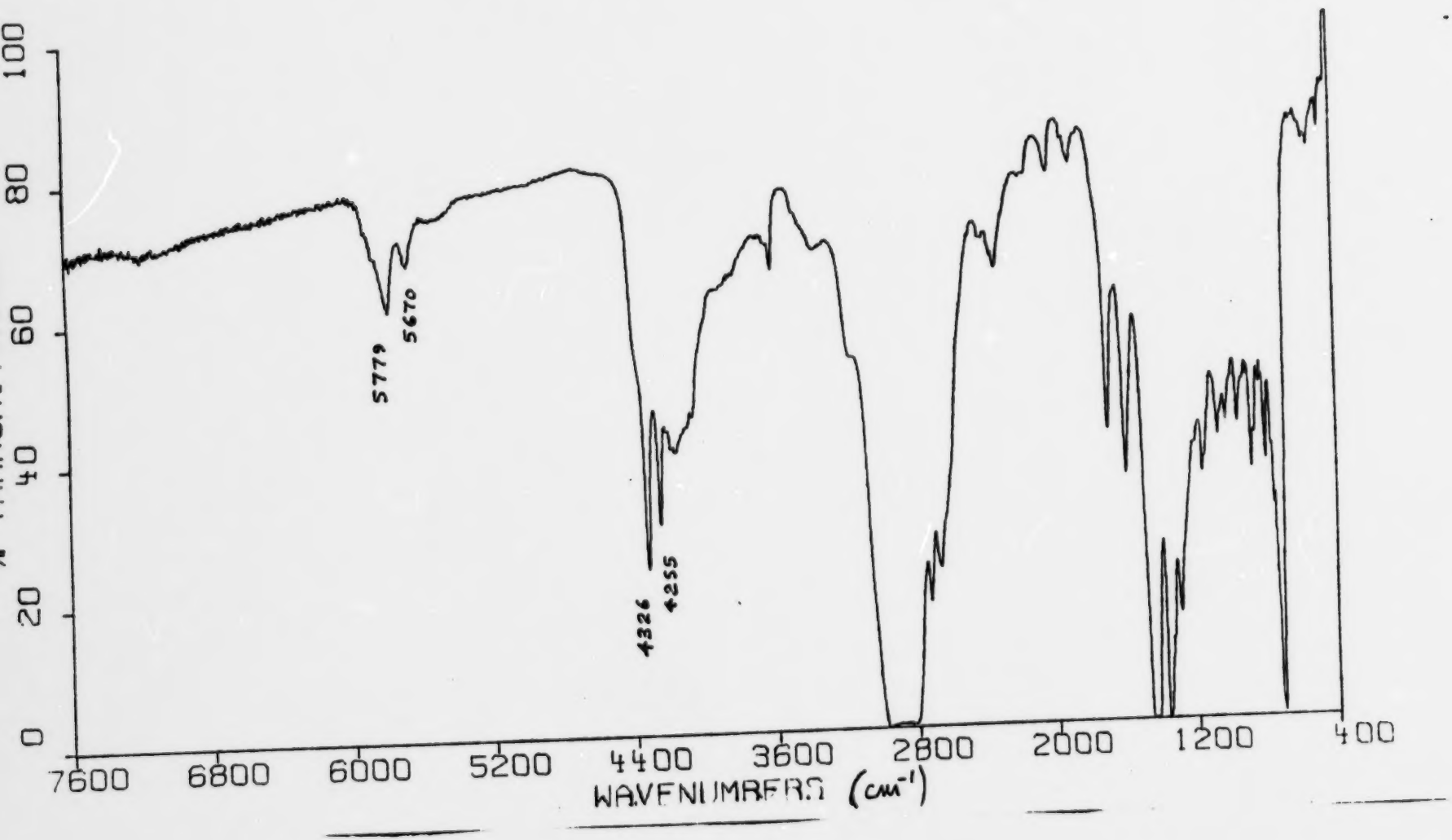

Figure 1: Transmission spectrum of "Bahia" crude oil, with a cell thickness of nearly 200 μm.

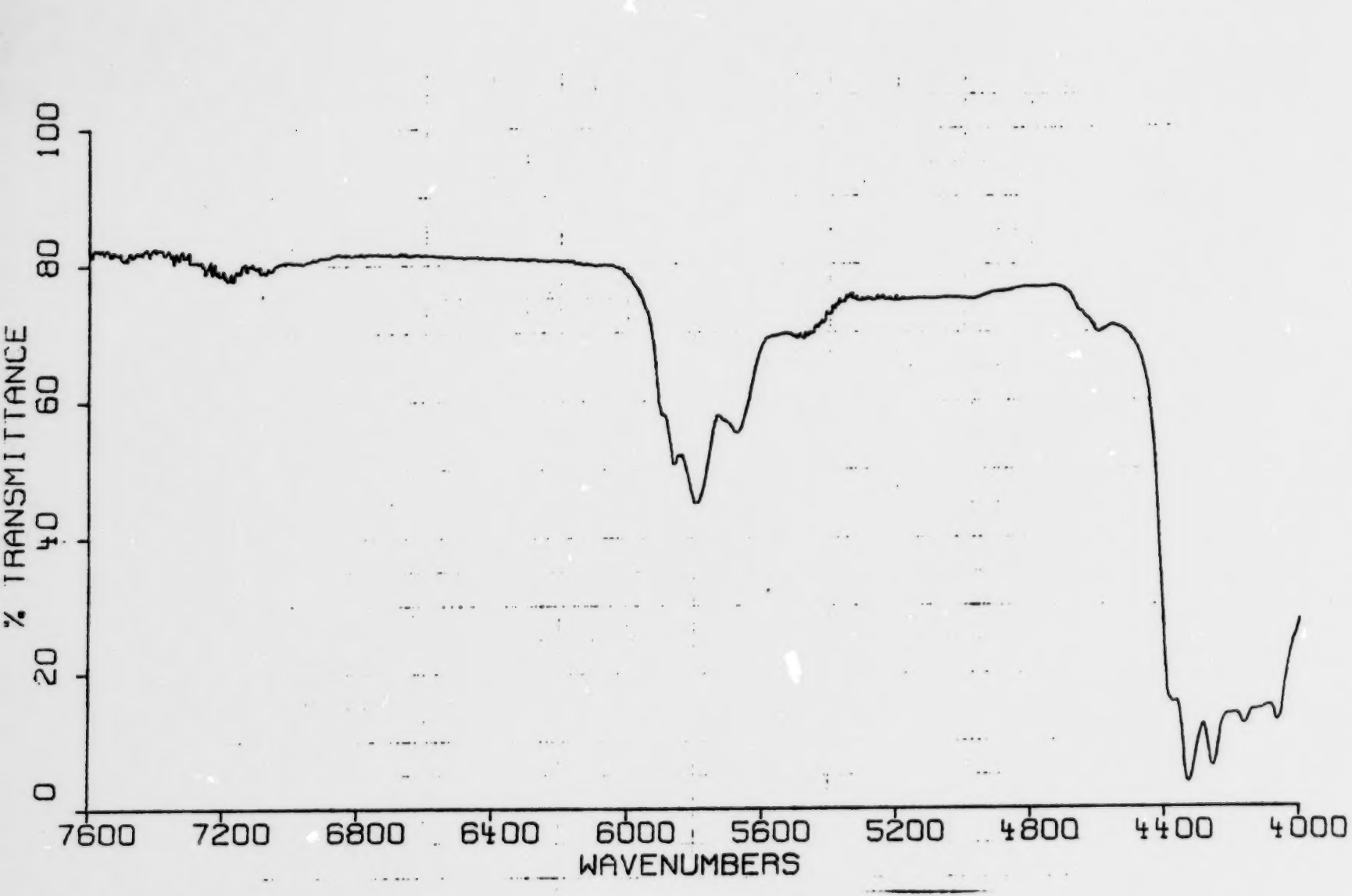

Figure 2: Near-IR transmission spectrum of the Esso-supplied crude oil sample. Cell thickness 0.5 mm.

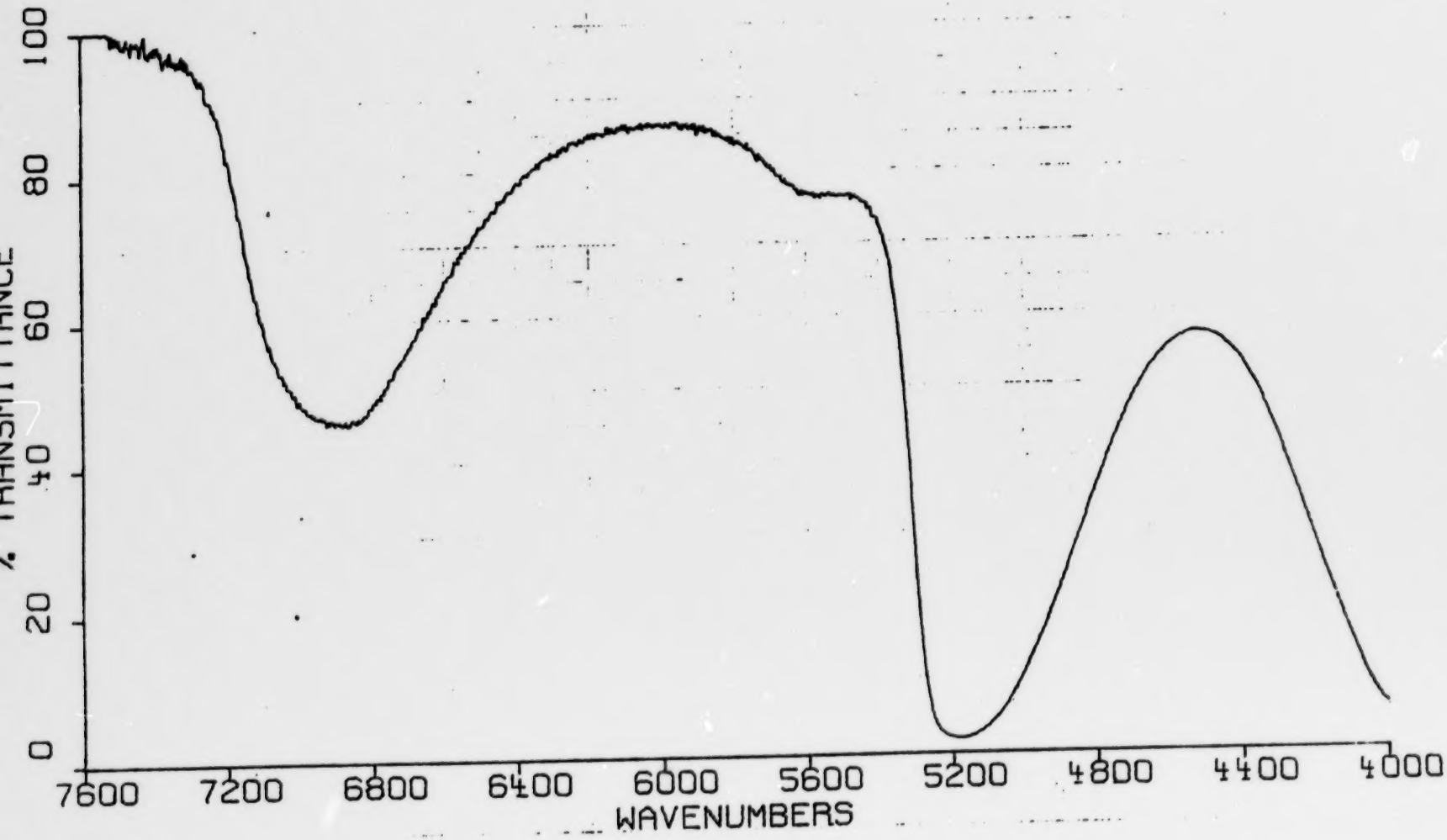

Figure 3: Near-IR spectrum of demineralized water, cell thickness 297 μm.

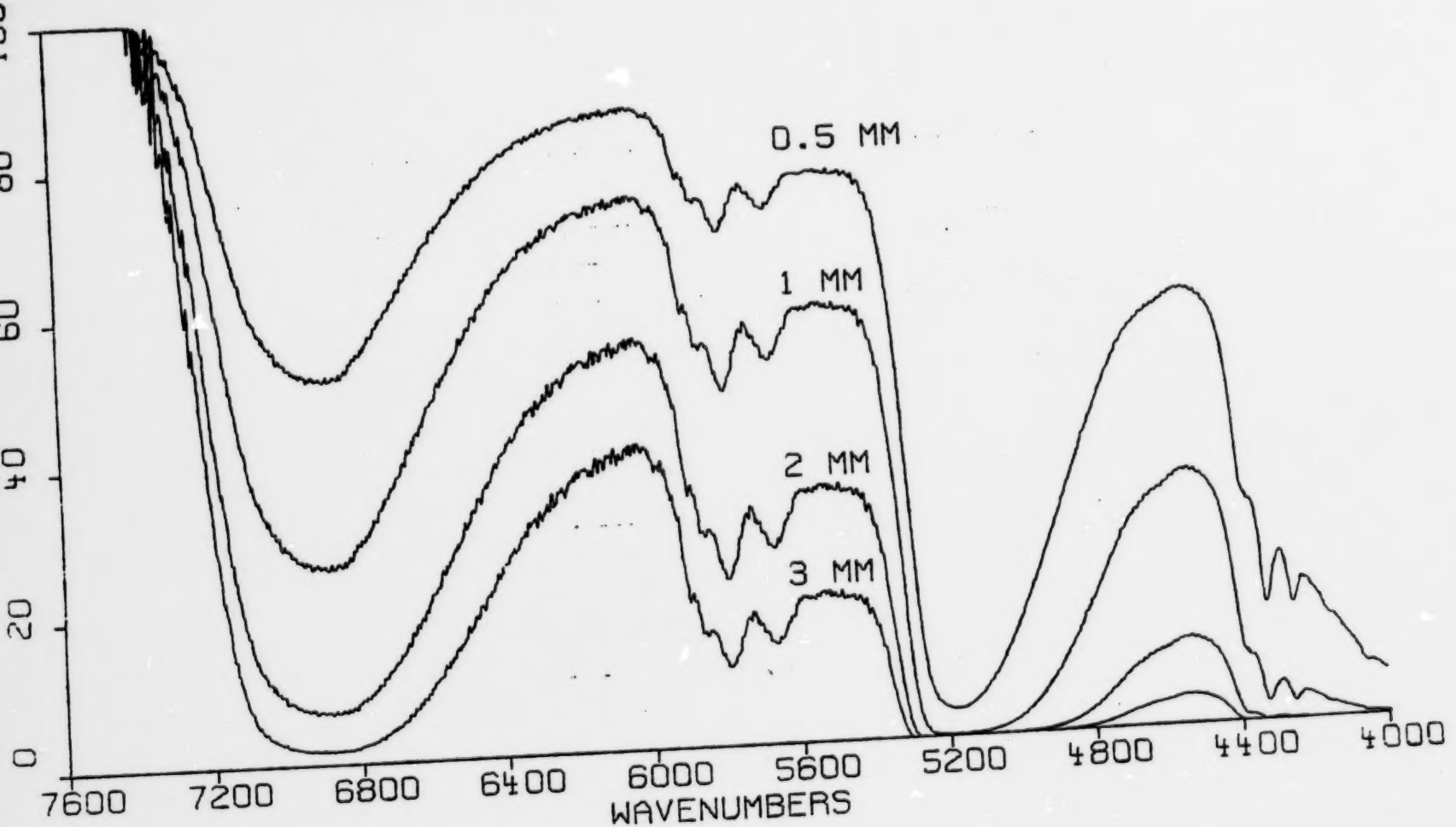

Figure 4: Projected spectrum of a 50:50 oil and water mixture for different cell thicknesses.

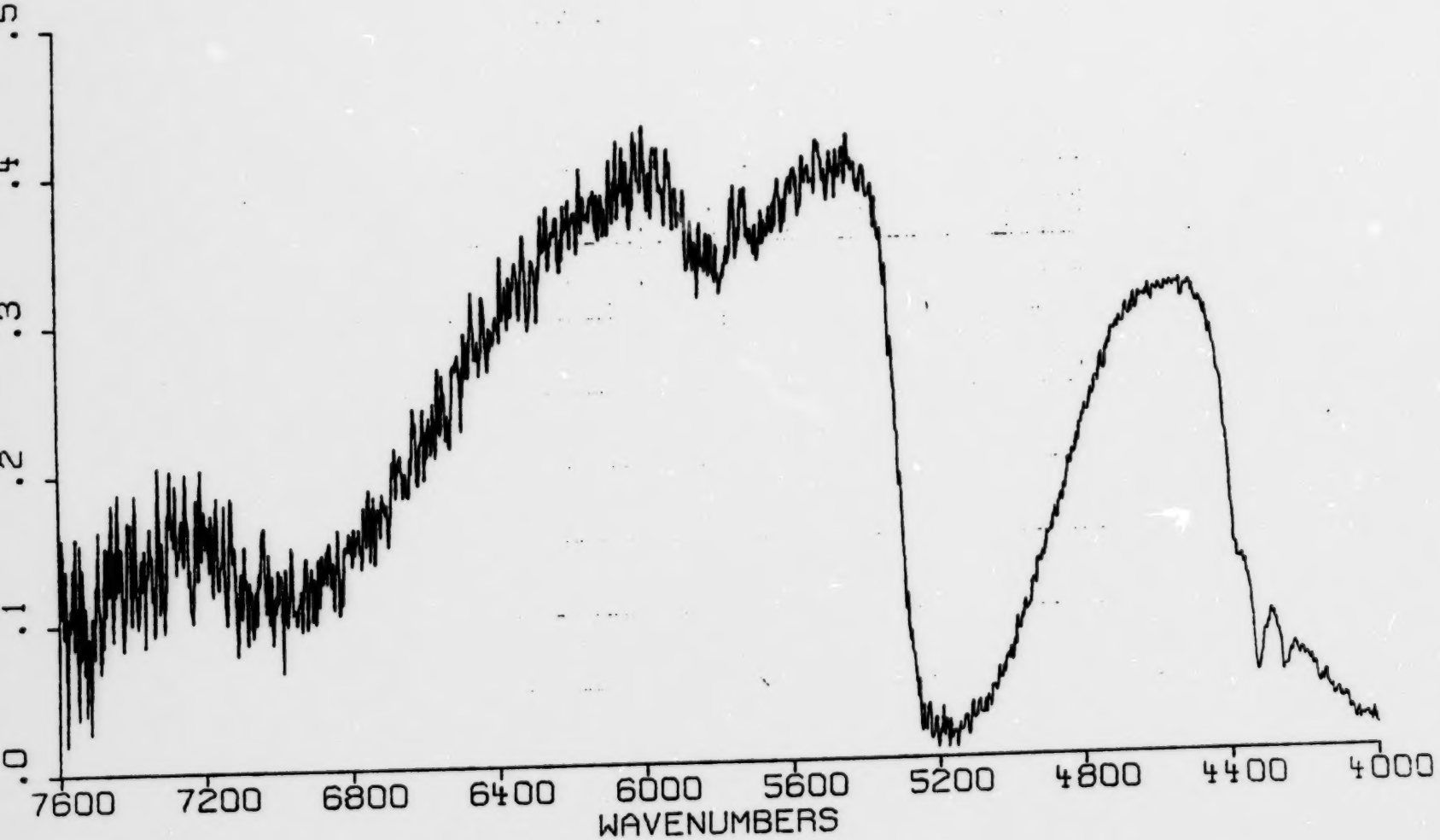

Figure 5: Transmission spectrum of a 50:50 oil/water sample after high speed mixing to obtain a fine emulsion. Cell thickness 0.5 mm.

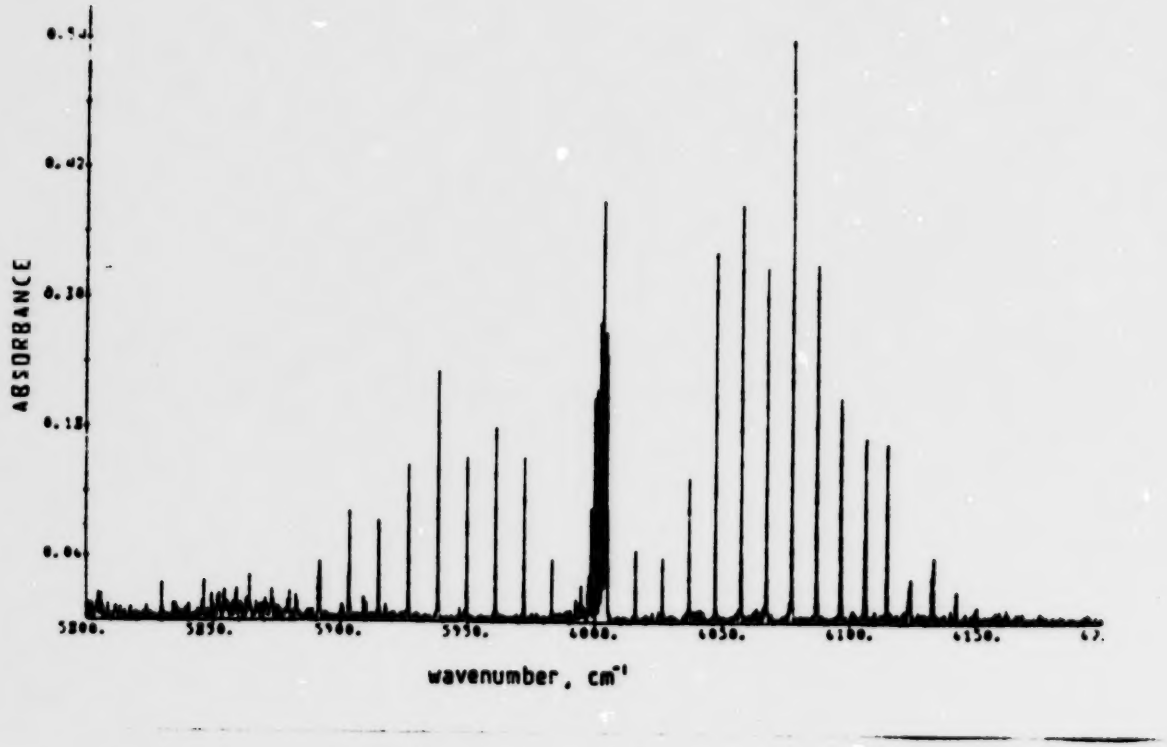

Figure 6: Near-IR absorbance spectrum of methane gas in a 500 mm cell (from Ref. 3).

APPENDIX I

Excerpts from the paper:

"Optical inspection for industrial quality and process control"

by P. Cielo, K. Cole and B. Favis

in: Instrumentation and Automation in the Paper, Rubber, Plastics and Polymerization Industries,

A. Kaya and T.J. Williams Editors,
IFAC Proc. Series, p. 161, Pergamon Press, Oxford, 1987

3.4 On-line polymer film thickness monitoring by spectrally-selective infrared transmissivity.

The thickness inspection of thin organic sheets, such as extruded polymeric sheets or blown-film polyethylene materials, is a problem of great concern for the plastics and rubber industry. A precise machine-direction thickness control is an important requirement for material savings considerations. Moreover, a departure from a uniform cross-machine-direction thickness profile indicates the presence of a process malfunction such as roller misalignment or an eccentricity of the concentric extruding dies in a film-blowing machine. A view of a polyethylene blown-film rotating extruder with the IMRI thickness monitoring prototype installed for double-thickness measurement of the folded plastics film is shown in Fig. 35.

Although a wide variety of physical approaches are possible for thickness measurement, (see,e.g., Ref. 3, Sects. 2-2 and 2-4), including electric capacitance, microwave attenuation, ultrasonic pulse-echo, etc., the most widely used methods for thickness measurement of thin plastics films are nuclear and infrared techniques. Nuclear sensors of the gamma-backscattering type can inspect plastics sheets of 5 μm to 100 μm in thickness, while higher-power X-ray transmission devices can be used for thicker sheets. Such instruments are, however, relatively expensive and have a number of limitations: they require frequent recalibration, must be installed in close proximity to the film, have a relatively slow response time, which is normally inadequate for machine-direction thickness fluctuation monitoring, and must be handled with care because of radiation hazards.

Infrared techniques[15] are increasingly used for monitoring the thickness of transparent films. Two typical configurations are shown in Fig. 36. In both diagrams, a light beam is transmitted through the film. A similar configuration is used in reflection for monitoring the thickness of coatings on opaque substrates. The film thickness is obtained by applying the law of Lambert to the absorbance of the film at two selective wavelengths (Ref. 3, Sects. 5.1.3 and 8.3.1).

Figure 37 shows the transmittance spectrum of a moderately-dyed, 15 μm-thick polyethylene film. Absorption regions around 2.4, 3.4, 7 and 13.7 μm are characteristic of the polyethylene molecular-vibration bands. By measuring the transmittance at about 2.1 μm and 2.35 μm, the absorbance and thus the thickness can be evaluated with rugged low-wavelength detectors and without being affected by the 1.9 μm and 2.7 μm moist-air absorption bands (see Fig. 38).

One of the problems encountered with films containing a large amount of light-scattering pigments or having a relatively rough surface finish is the wavelength dependence of the scattering-related attenuation in the transmitted or reflected light beam. As shown in Fig. 39, scattering losses are higher at low wavelengths when a large amount of pigment is present in the film. The dependence of the scattering losses upon the light wavelength is strikingly apparent in Fig. 40, showing the transmittance spectrum of a heavily pigmented, black-carbon-filled film. If the thickness is evaluated by simply taking the ratio between the transmittivities at, e.g., 2.1 μm and 2.35 μm, Figs. 39 and 40 show that the estimated thickness value will be smaller than the real value when the scattering-related attenuation is of the same order of magnitude as the absorption-related attenuation. Better thickness evaluation can be obtained independently of the scattering level by measuring the transmittance at three wavelengths, e.g. 2.05 μm, 2.2 μm and 2.35 μm, and using the two signals detected at the lower wavelengths to extrapolate the transmittance before absorption at 2.35 μm, as shown by the dotted lines in Fig. 39. By applying the three-wavelength method (Fig. 41), the measured absorbance at 2.35 μm became linearly related to the film thickness. Such a technique gives a much better precision while making the measurement independent of the scattering properties of the inspected material. Similar pigment or surface-finish independent results were obtained in a reflective configuration of the kind shown in Fig. 42.

Figure 37 also shows the presence in the 3.5 to 10 μm spectral region of some interference fringes due to multiple reflections within the film. Such fringes are particularly evident in the longer-wavelength spectral region where the surface-roughness amplitude becomes small with respect to the optical wavelength. The contrast and position of the fringes is also dependent on the angle of incidence and on the angular aperture of the inspecting device. For smoother films, the presence of fringes in the low-wavelength region is a major cause of noise in the evaluation of the absorption-peak depth. Several methods can be used to minimize the interference fringes[16], such as using larger angular apertures or oblique angles of incidence or else superposing both the transmitted and reflected light beams which have reversed fringe patterns. Another approach is to use the fringe information to better estimate the film thickness from a knowledge of the angle of incidence and of the film refractive index[17]. The fringe visibility can be improved by properly processing spectrograms obtained separately with light polarized in the two normal planes.

Such an approach will now be illustrated with reference to a coating inspection problem. Plastics-coated steel sheets were to be inspected for coating thickness by a magnetic-steel manufacturer. A feasibility study using the spectral approach in reflection was performed at our institute on samples with coating thickness ranging from 2.5 to 25 μm using an FTIR spectrometer. A typical spectral distribution of the light reflected from the coated-steel surface is shown in Fig. 43. This spectrum is difficult to interpret because of the presence of multiple-reflection interference fringes which interfere with the absorption peaks, as well as of a number of distortions related to instrumental parameters such as the spectral radiant emittance of the source, the spectral sensitivity of the detector and the presence of absorption bands from water vapor and carbon dioxide in the atmosphere.

The signal fluctuations produced by the interference fringes can be separated from the other features of the spectrum by operating at polarized-light conditions near the Brewster angle of incidence (nearly 50 degrees, see Fig. 44). Figure 45 shows the normalized spectra obtained in the same conditions as in Fig. 43 but with a polarizer inserted across the light beam so that the polarization vector was (a) perpendicular (S-polarization), or (b) parallel (P-polarization) to the plane of incidence. In the S-polarization case, Fig. 45(a), the reflection at the coating-to-steel interface interferes with a strong air-to-coating reflection to produce a high-contrast interference-fringe pattern. In the P-polarization case, Fig. 45(b), no reflection takes place at the air-to-coating interface at the Brewster angle, so that no interference fringes are present. The film thickness can thus be reliably evaluated either from the depth of the 2900 cm^{-1} absorbance peak in the P-polarized spectrum of Fig. 45(b) or by measuring the interfringe in the S-polarized spectrum shown in Fig. 45(a).

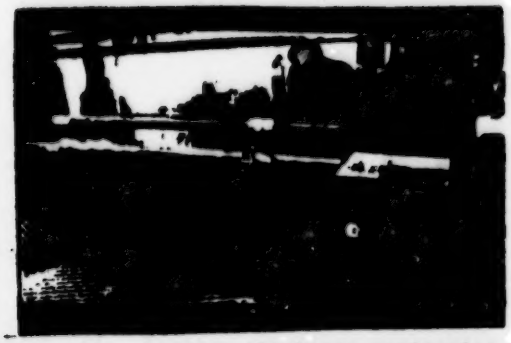

Figure 35: On-line thickness monitoring of a blown-film extruded polyehtylene sheet.

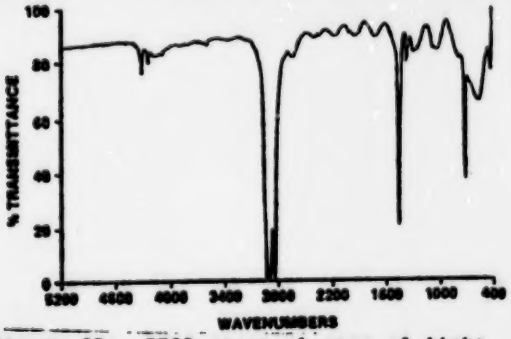

Figure 37: FTIR spectral scan of light transmitted trhough a 15 μm-thick polyethylene film.

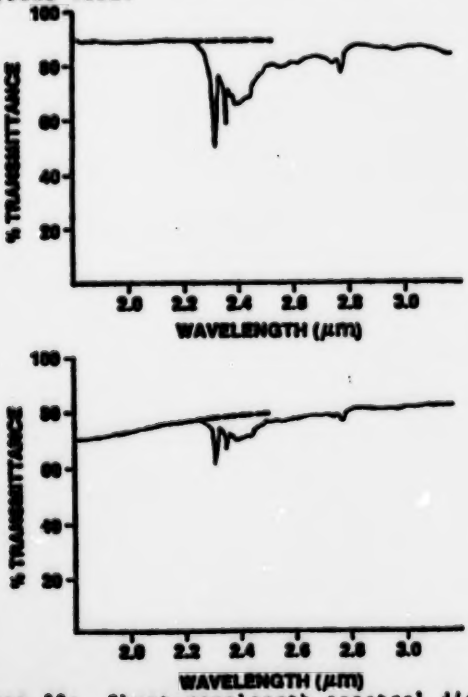

Figure 39: Short-wavelength spectral distribution of the light transmitted through a clear-plastics, 65 μm-thick film (top) and a white-pigmented, 20 μm-thick film (bottom).

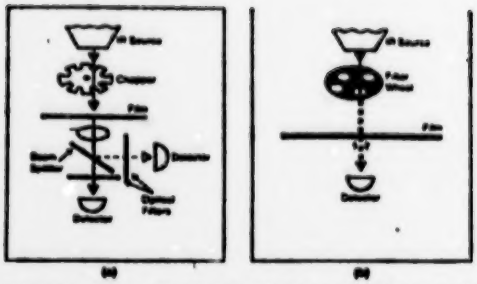

Figure 36: Typical infrared-absorption configurations for monitoring film-thickness by (a) simultaneous comparison of transmissivity of two wavelengths and (b) sequential analysis of spectral transmissivity.

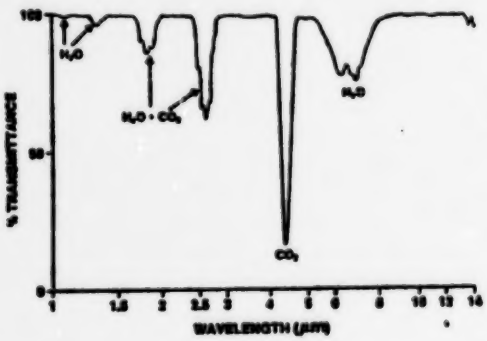

Figure 38: Infrared transmission through 1 m of air at standard conditions.

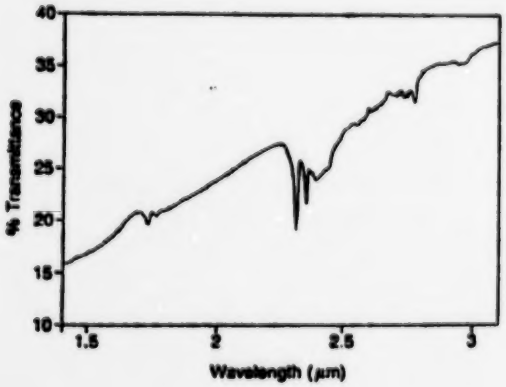

Figure 40: Spectral distribution of the light beam transmitted through a black-carbon pigmented, 50 μm-thick polyethylene sheet.

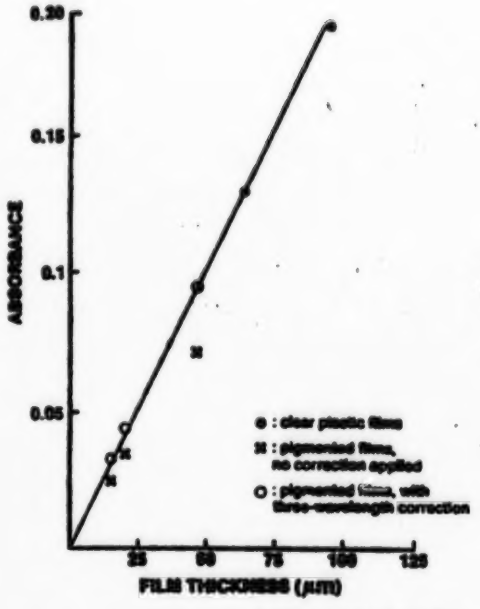

Figure 41: Correlation between the experimentally-measured absorptance and the film thickness for several polyethylene films with or without scattering pigments, before and after three-wavelength correction.

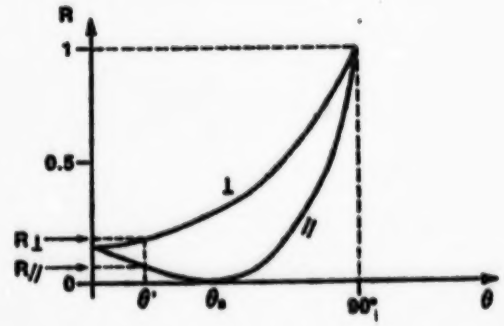

Figure 44: Fresnel reflectivity vs. angle of incidence at an air-plastics interface, for light polarized in a direction parallel or perpendicular to the plane of incidence.

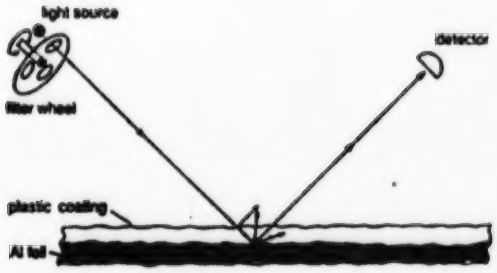

Figure 42: Setup for coating thickness measurement.

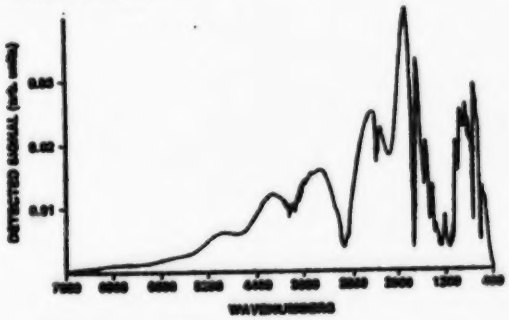

Figure 43: Spectral distribution of the light reflected from a steel sheet with a 4.75 μm-thick polymeric coating at 57° incidence.

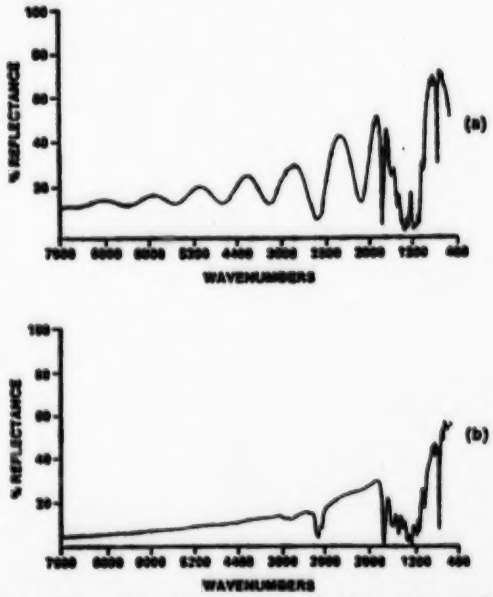

Figure 45: Spectra obtained with the same sample as for Fig. 43 but using light polarized in a direction (a) perpendicular and (b) parallel to the plane of incidence. The spectra were normalized through division by the respective neutral-mirror reference curves.